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Final Report

HIGH ENERGY OXIDIZERS IN SOLUTION (U)

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AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA

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HIGH ENERGY OXIDIZERS IN SOLUTION (U)

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SRI Project FRU 4566

Approved: N. K. HESTER, DIRECTOR
CHEMICAL SYNTHESIS & DEVELOPMENT DIVISION

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FOREWORD

This final report was prepared by Stanford Research Institute, Menlo Park, California, under Contract AF 04(611)-9370 for the Air Force Rocket Propulsion Laboratory, Edwards, California. The report covers the period from July 1, 1963, to August 15, 1966, with major emphasis on the research of the past year. The program was sponsored by the Advanced Research Projects Agency under ARPA Order 24, Amendment 64, Task 16, Program Code 391, Program Structure 920F, Project AFSC 4981. Scientists who worked on the program included Marion E. Hill, project supervisor; W.E. Tolberg and R.T. Rewick, principal investigators; R.S. Stringham, J.A. Neff, inorganic chemists; and C.A. Crutchfield, Anna Longwell, Ruth McNeely, and Ena Viale, analytical chemists. The technical consultation of Dr. Henry Taube of Stanford University is gratefully acknowledged.

The Air Force Rocket Propulsion Laboratory Contract Monitor is Dr. William Leahy/RPCL.

This technical report has been reviewed and is approved.

W.H. Ebelke, Colonel, USAF
Chief, Propellant Division

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CONTENTS

I INTRODUCTION AND SUMMARY

This is the Final Report on Contract AF 04(611)-9370 which has been completed and has been succeeded by Contract F 04611-67-(C)-0092. The report, which contains unpublished work and four manuscripts for publication, summarizes research carried out in the period from July 1, 1963, to August 15, 1966, with major emphasis on the results obtained since May 1965. The highlight of this work was the discovery of the NF_4^+ cation described in Article 1, "The Synthesis of the Perfluoro Ammonium Cation, NF_4^+," a manuscript in process of publication in Inorganic Chemistry. Preliminary notice of the discovery of NF_4^+ was published in a communication to Inorganic and Nuclear Chemistry Letters, which is reproduced here as Article 2.

The research in this program had two objectives. The first was to determine whether energetic ionic species could be synthesized in chemical systems consisting of very weak bases such as NF_3 and very strong acids such as SbF_5. The new species, if formed, were expected to be energetic cations associated with the corresponding anions such as SbF_6^-. The second objective was to carry out the synthesis of highly energetic salts by coupling the new energetic cations with energetic anions through metathetical reactions in the solvent anhydrous HF.

The chemical system $NF_3/F_2/SbF_5/HF$ was selected for study as being the most likely to be capable of forming the desired new cations. It was expected that, in the combinations of reagents containing NF_3, one or more of the ions, NF_x^+, could be synthesized. New information coincidental to these studies is reported in Article 3 "Evidence for the Existence of the $Sb_2F_{11}^-$ Anion" and in Article 4 "The Solubility of F_2, NF_3, and O_2 in Anhydrous Liquid HF" which will be submitted to Inorganic Chemistry and to Chemical and Engineering Data, respectively.

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The quaternary system as well as its four ternary and six binary subsystems have been studied extensively and, as a result, a number of new salts containing energetic cations have been synthesized. The most important and most thoroughly characterized of these is the new salt, NF_4SbF_6, containing the energetic cation NF_4^+. It has been synthesized in greater than 10-gram quantities having purities from 96 to 99%. The salts $NF_4Sb_2F_{11}$, $NF_4Sb_3F_{16}$, and NF_4AsF_6 have also been synthesized and characterized. In addition, partial evidence for the formation of a very small quantity of the new salt $NF_2^+Sb_2F_{11}$ has also been obtained.

The above results have satisfied the first objective of the research. Additional results have established the feasibility of achieving the second. It has been shown that NF_4SbF_6 and $KClO_4$ in solution in HF are not mutually destructive and therefore that the synthesis of NF_4ClO_4 is, in principle, possible.

The remainder of this report consists of one section containing classified information and four manuscripts intended for publication in various journals.

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II UNPUBLISHED RESULTS

The Reaction of NF_3 with SbF_5

Because the reaction of NF_3, F_2, and SbF_5 produces NF_4SbF_6, it was clearly possible that the reaction of NF_3 and SbF_5 would produce NF_2SbF_6. This possibility follows from the fact that the presence of NF_2^+ is implied in one of the two mechanisms that have been deduced as leading to the formation of NF_4^+. The pertinent mechanism is:

$$NF_3 + SbF_5 \rightarrow NF_2SbF_6$$

$$NF_2SbF_6 + F_2 \rightarrow NF_4SbF_6$$

The alternate route is:

$$F_2 + SbF_5 \rightarrow F^+SbF_6^-$$

$$NF_3 + F^+SbF_6^- \rightarrow NF_4SbF_6$$
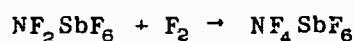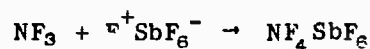
The first of these two routes was studied by heating NF_3 and SbF_5 at $200^{\circ}C$ and 2400 psi for 50 hours. The quantity of gas isolated from the reaction mixture was only slightly less than that initially present. The gas contained, however, a small amount of a material that was not condensable in liquid nitrogen. This appeared to be nitrogen because its vapor pressure at $-210^{\circ}C$ was higher than that of F_2, the only possible alternative. It was also found that slightly more than 2% of the NF_3 had disappeared. From this evidence it was clear that a reaction of NF_3 had occurred and that nitrogen gas had formed. We detected no N_2F_4 or N_2F_2 in the infrared spectra of the condensable fraction. These gases, if present, might have formed antimonate complexes in the presence of SbF_5. The excess SbF_5 was removed from the reactor at $50^{\circ}C$, a temperature that would not decompose such complexes.

When the reactor was cut open in a dry box, a quantity of a white solid was found on the walls of the lower part of the vessel. This material was hydrolyzed and the gas evolved was analyzed by mass spectrometry. The gas contained O_2, NF_3, NO_2, NO, and N_2O. The

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hydrolysate contained a substantial quantity of nickel and copper salts, implying the presence of Ni(II) and Cu(II) antimonates in the white product.

The presence of NF_3 and O_2 in the gas evolved on hydrolysis indicated the presence of NF_4^+. The oxides of nitrogen formed indicated the possible presence of the antimonate complexes of N_2F_4 and N_2F_2 and of NF_2^+ whose reaction with water would produce oxides of nitrogen of the same valence state.

We regarded it as highly unlikely that NF_3 would disproportionate to the elements and to N_2F_4 and N_2F_2 in a heavily passivated vessel at $200°C$. Thus it appeared likely that the first step in the observed reaction was:

$$NF_3 + 2SbF_5 \rightarrow NF_2^+Sb_2F_{11}^-$$

From the unusually large amount of monel salts formed, it was concluded that a second reaction was:

$$NF_2^+ + Ni \rightarrow NiF_2 + \tfrac{1}{2}N_2$$

The formation of NF_4^+ could be accounted for as follows:

$$NF_3 + NF_2^+ \rightarrow NF_4^+ + \tfrac{1}{2}N_2F_2$$
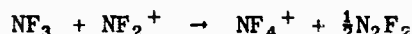
On the basis of these reactions and with the assumption that disproportionation of NF_3 did not occur, we concluded but did not prove that NF_2^+ had been formed. The study of this reaction was not pursued further because of the apparent lower stability of the product formed as compared with NF_4^+.

Interaction of a Perchlorate with NF_4SbF_6

We attempted to determine whether the synthesis of NF_4ClO_4 is possible, first by observing the stability of a mixture of the solids NF_4SbF_6 and $KClO_4$, and second by observing the behavior of these two solids in solution in liquid HF. Because no apparent mutual destruction of the perchlorate and NF_4SbF_6 was detected, in our opinion synthesis of NF_4ClO_4 should be possible.

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It has been reported[1] that attempts to prepare $NF_2O^+ClO_4$ resulted in mutual destruction of NF_2O^+ and ClO_4^- to form $FClO_3$ and FNO_2. In our experiments involving NF_4SbF_6 and $KClO_4$, we searched the contents of the reaction vessel for evidence that would indicate the occurrence of such a decomposition. No molecules containing the species F-Cl-O or F-N-O were found either in the gas phase or in successive fractions obtained by vaporizing the HF solvent. The solid remaining after removal of solvent was hydrolyzed; no evidence for the presence of nitrogen oxides could be observed, although evolved gas (presumably NF_3 and O_2) indicated the presence of the NF_4^+ cation in the residue.

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[1]Allied Chemical Corporation, General Chemical Division, Quarterly Report No. PR-25, Contract No. DA-01-021-AMC-12264(Z), June 1965.

Article 1

THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, NF_4^+

THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, NF_4^+

W.E. Tolberg, R.T. Rewick, R.S. Stringham, and M.E. Hill

ABSTRACT

When a mixture of nitrogen trifluoride, fluorine, and antimony pentafluoride is heated under pressure, the salt NF_4SbF_6 is formed. This is the first derivative of the perfluoroammonium cation NF_4^+ to be observed. It was characterized by evidence obtained from thermal decomposition, hydrolysis, elemental analyses, and fluorine nmr spectra. The salt is stable in a very dry atmosphere and at $200°C$ _in vacuo_ but decomposes rapidly above $300°C$ to NF_3, F_2, and SbF_5. Elemental analysis was carried out by determination of the quantity and identity of the gases evolved on hydrolysis followed by analysis of the hydrolysate. Hydrolysis of NF_4^+ quantitatively produces NF_3 and O_2 in a two to one mole ratio. These analyses showed that the empirical composition of the solid was $NSbF_{10}$, and that the oxidation number of nitrogen in the compound is five. The product is from 96 to 99% pure as isolated from the monel reactor, the balance consisting mainly of $Ni(SbF_6)_2$. The fluorine nmr spectra were obtained from the salt dissolved in anhydrous HF and were consistent with the presence of SbF_6^- and of a species of the type $NF_x^{\pm,0}$. From this and other evidence the structure of the salt was shown to be $NF_4^+SbF_6^-$. Because the nmr spectra showed that all fluorines attached to nitrogen are equivalent, the NF_4^+ ion is almost certainly tetrahedral.

The salt NF_4AsF_6 was also synthesized in a similar reaction and was characterized by thermal decomposition, hydrolysis, and elemental analysis. These results were quite analogous to those of the antimonate salt except that the thermal decomposition temperature was slightly lower and the purity was only about 95%.

INTRODUCTION

In a recent communication,[1] the synthesis of the new cation NF_4^+
was described as resulting from the reaction of nitrogen trifluoride,
fluorine, and antimony pentafluoride in liquid HF, at $200^\circ C$ and up to
85 atmospheres pressure in a monel metal vessel. The product consisted
of a mixture of NF_4SbF_6 and the antimonate and fluoride salts of metals
from the reaction vessel.

This synthesis resulted from a systematic study of the $NF_3/F_2/SbF_5/HF$
system in which it was thought that one or more of the possible NF_x^+
cations might be formed from NF_3. We have studied extensively a number
of combinations of the components of the above quaternary system and
and have found, in addition to the reaction reported earlier, a second
reaction in which the NF_4^+ cation is formed. These two reactions differ
in that, in the first, a liquid phase of HF was present while, in the
second, no HF was added to the system. The new reaction is:

$$NF_3 + F_2 + SbF_5 \longrightarrow NF_4SbF_6 \qquad (1)$$
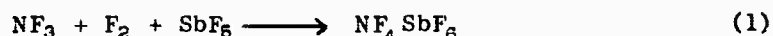
Price et al.,[2] on considering the NF_4^+ cation theoretically, con-
cluded from its calculated electron affinity and size that it could not
form crystalline salts. Wilson[3] estimated the heat of formation of NF_4^+
by comparing the isoelectronic series $CF_2/CF_3/CF_4$ and $NF_2^+/NF_3^+/NF_4^+$.
From this and other considerations, he concluded that it was not unlikely
that NF_4^+ could be prepared by a suitable ion-molecule reaction and
observed in the gas phase. He also discussed the stability of
hypothetical perfluoroammonium fluoride, perchlorate, sulfate, and
fluoborate. Of these, only the latter was thought possibly capable of
existence and this only at low temperatures. He did not discuss the
antimonate or arsenate salts in his paper but privately stated that these
might very well be stable.

Prior to our experimental studies of the $NF_3/F_2/SbF_5/HF$ system, we
concluded that, if the series, BF_4^-, CF_4, NF_4^+, and their trifluoride
precursors had consistent properties, NF_4^+ might be considerably more

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stable than predicted. We also estimated the heat of reaction to form the hypothetical salt $NF_4^+F^-$ in liquid HF.[4] These conclusions and calculations encouraged us to attempt the preparation of NF_4SbF_6.

Nearly pure NF_4SbF_6 can be obtained under certain conditions. Variation of temperature and heating periods has produced salts having the compositions $NF_4Sb_2F_{11}$ and $NF_4Sb_3F_{16}$. It is likely that the complex anions $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ exist in these salts, since the fluorine nmr spectrum of $Sb_2F_{11}^-$ has been observed in other systems.[5,6,7] NF_4SbF_6 can be obtained from these salts, however, by heating them in vacuo.

The following describes the preparation, characterization, and some reactions of NF_4SbF_6 and NF_4AsF_6.

EXPERIMENTAL SECTION

Apparatus. The vacuum system used in this work consisted of a metal manifold to which a number of subsystems were attached. These were: (1) a multipurpose line for handling, measuring, and transferring reactants; (2) a line for purifying and storing fluorine; and (3) a similar line for nitrogen trifluoride. The multipurpose subsystem (1) with a monel metal reaction vessel attached is shown in Figure 1 and the fluorine line in Figure 2.

All valves are Hoke M-482-M bellows valves. The fluorine line consists of copper lines and vessels fabricated with silver/copper eutectic solder. The multipurpose line is of monel metal assembled by means of heliarc welding. Demountable joints were made from fittings having FEP Teflon ferrules.

The 60-cc reaction vessel is shown in detail in Figure 3. The vessels were fabricated by means of heliarc welding and were tested under vacuum with a helium leak detector, treated with fluorine gas, and later tested at 200 atmospheres with nitrogen gas. The welds are made the full thickness of the tubing for strength.

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FIG. 1 MULTIPURPOSE LINE

SCRUB VAC

VAC

F₂ SUPPLY

F₂ TO SYSTEM

COMPOUND GAUGE
TO 100 psi

0-30" VAC

I LITER METERING
VOLUME

PACKED TRAP

0-100 psi

I LITER STORAGE
VESSEL
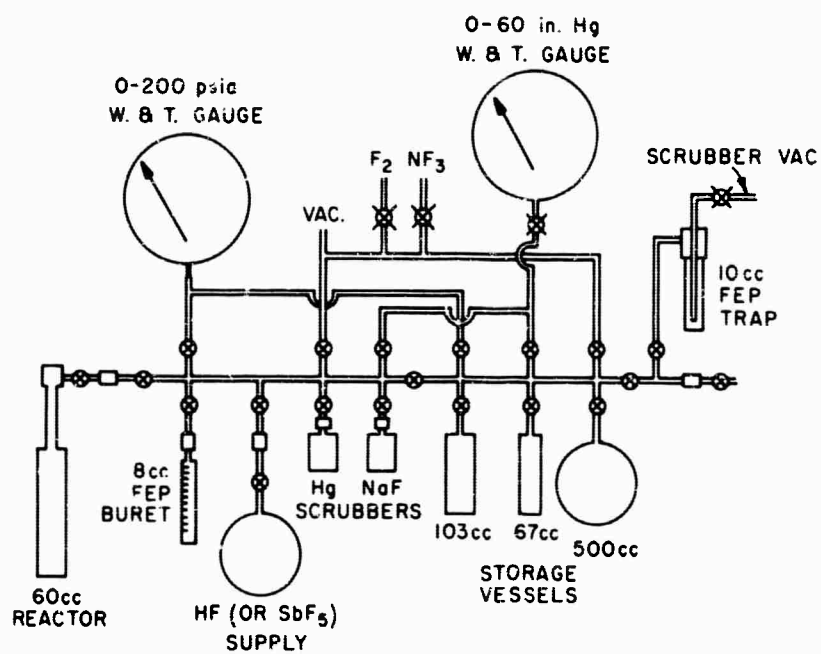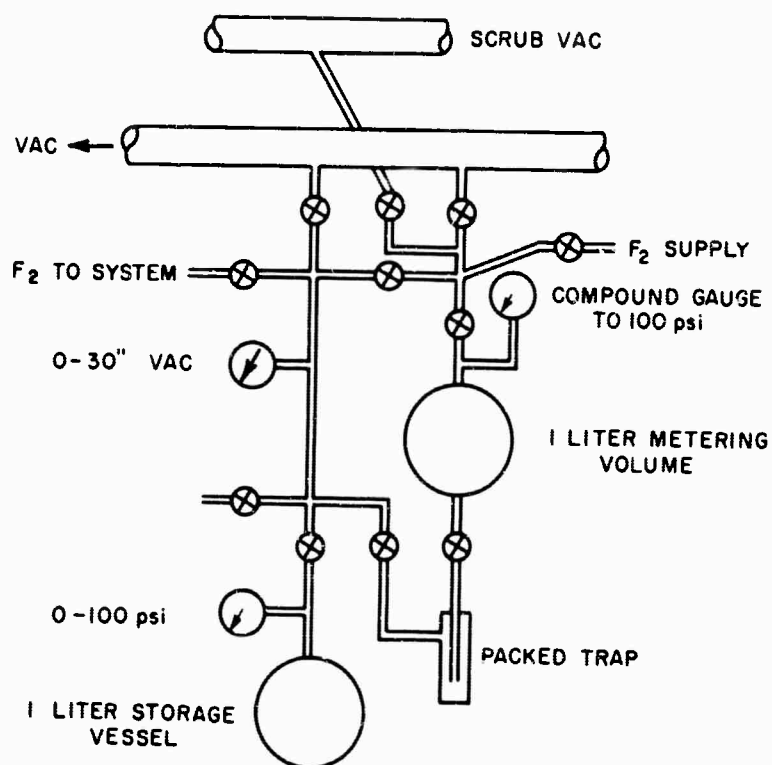
TA-4566-38

FIG. 2 FLUORINE PURIFICATION LINE

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FIG. 3 MONEL REACTION VESSEL

TA-4566-37

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Reagents. Nitrogen trifluoride was obtained 99.9% pure from Air Products Company. Because about 0.1 mole or 7 grams were required for each preparation, the NF_3 was transferred within the vacuum system by a method designed to prevent contamination and to remove the nitrogen impurity originally present. Two and one fourth liter-atmospheres was condensed at liquid nitrogen temperature, warmed to -130°C, and transferred to the calibrated volume at -196°C and pumped on.

Fluorine with a typical analysis of 98% purity was obtained from Allied Chemical Corporation. Three liter-atmospheres was condensed into a trap packed with nickel spirals and cooled to -196°C. The gas remaining in the metering volume was isolated from the trap, and the contents of the trap volatile at -196°C were transferred to a 1-liter volume cooled to -210°C. On isolation from the trap, the liquid was pumped on at -210°C (solid nitrogen/liquid nitrogen slush), warmed to -196°C, and transferred into the calibrated volume at -210°C.

Antimony pentafluoride was obtained 99.5% pure from Allied Chemical Corporation. It was transferred directly from the supply vessel into an FEP Teflon buret by trap-to-trap distillation. The contents of the buret were pumped on at -44°C and used without further purification.

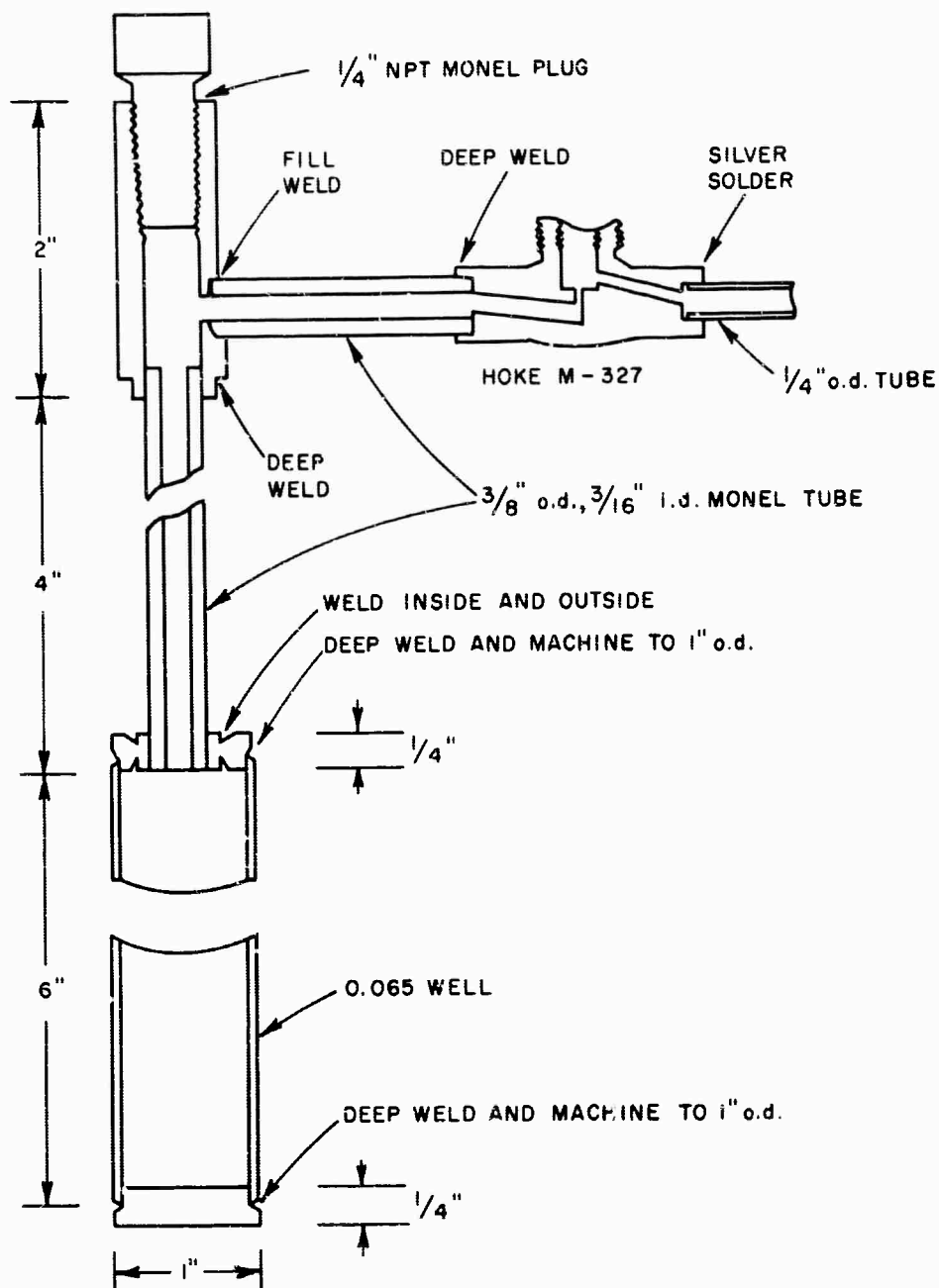Hydrogen fluoride was obtained in excellent purity from Olin Corporation. Because HF reacts slowly with its container forming hydrogen gas, the hydrogen must be removed both to facilitate vacuum transfer and to avoid reaction with fluorine on subsequent fluorination of the HF. In addition, solid HF expands rapidly on melting, and at 23°C the resulting liquid occupies a volume about 1.5 times that of the solid. Therefore, an enclosed container filled with solid HF will burst as the HF melts. Figure 4 shows the apparatus used to obtain about 200 cc of solid HF in a double trap that is pumped on while cooled with liquid nitrogen. The HF is transferred successively from the trap to the buret and to the storage vessel where it is treated with fluorine gas. The fluorine is removed by pumping on the HF cooled to -196°C.

Experimental Techniques. The volumes of all sections of the multi-purpose line were measured by expansion of a known pressure of nitrogen

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SCRUB VAC

COMPOUND GAUGE

VAC

F_2

VENT

200 cc CAPACITY

HF

KEL-F BURET

DOUBLE TRAP

500 cc Cu STORAGE FLASK
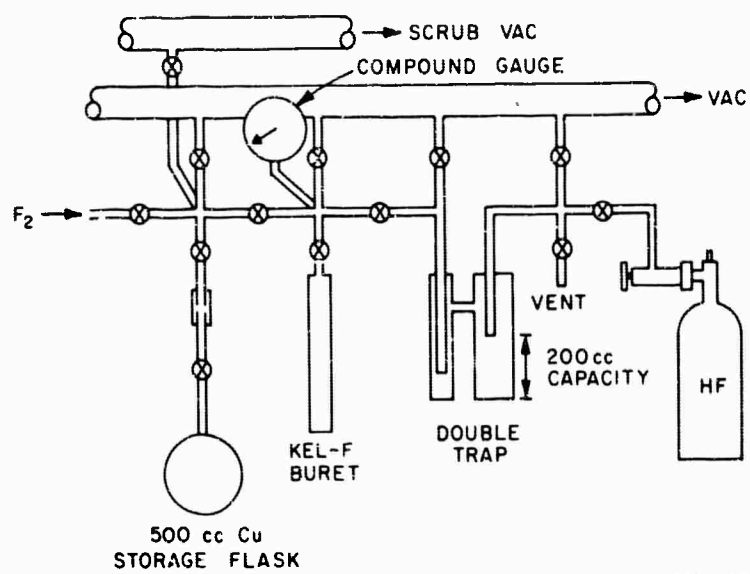
TA-4566-36R

FIG. 4 HF LINE

from a known volume. The vacuum system was maintained leak-free by testing with a helium leak detector. The combination of reagents HF, F_2, and SbF_5, although highly corrosive, appears to passivate the system. If exposed to air containing water vapor, the system corrodes and the bellows deteriorate rapidly. Thus, the bellows are never needlessly exposed to air and are installed so that they are in vacuum. All sections are treated with fluorine gas after each exposure to air.

Fluorine behaves as a perfect gas relative to its behavior at one atmosphere up to a pressure of 13 atmospheres (gauge limit), and was measured in the calibrated volume at sufficient pressure to obtain about 0.13 mole.

Nitrogen trifluoride does not behave as a perfect gas at pressures up to 13 atmospheres relative to its behavior at one atmosphere. Consequently, its deviation from perfect gas law behavior was determined and used to obtain measurement of the quantity of NF_3 supplied to the reaction vessel.

Antimony pentafluoride was measured only approximately by volume because in a metal system treated with fluorine much SbF_5 is lost by reaction with metal fluorides to form antimonate salts. The monel reaction vessel also absorbed several grams of SbF_5 when exposed to fluorine at high pressure and $200^\circ C$.

In a typical preparation, 0.07 mole SbF_5 and 0.09 mole NF_3 were condensed into the reaction vessel at $-196^\circ C$ while 0.13 mole of F_2 was condensed from the calibrated volume at $-196^\circ C$ into the reaction vessel at $-210^\circ C$. The reaction vessel was placed in a vertical tube furnace surrounded by Fiberglas and enclosed in a steel safety shield. The temperature was obtained from an iron-constantan thermocouple. The reaction mixtures were heated at $100^\circ C$ or at $200^\circ C$ for from 24 to 124 hours.

ANALYSES

The procedure is here outlined for safely removing unreacted starting materials from the reactor on completion of the heating period id for subsequent analysis of the NF_4^+ salts formed in the reaction. After 50 hours heating at $200^{\circ}C$, the reaction vessel is cooled and installed as shown in Figure 1. The sections of tubing exposed to the atmosphere are repassivated with fluorine gas, evacuated, and tested with a helium leak detector. The pressure of unreacted F_2 and NF_3 in the reaction vessel is in excess of 30 atmospheres. Because fluorine at pressures greater than two atmospheres cannot always be released through a small valve into an evacuated system without the occurrence of a fluorine fire in the valve, the reactor is cooled to $-196^{\circ}C$, the valve is opened, and the reactor is warmed to $-130^{\circ}C$. The F_2 and NF_3 are transferred into the 500-cc vessel and warmed to room temperature, and the pressure is recorded.

The mixture is condensed again in the 500-cc volume at $-210^{\circ}C$ and the fluorine is removed by pumping on the system. The fluorine is disposed of slowly through the scrub vacuum line which is equipped with a Sodasorb trap. Complete separation of fluorine requires repeated warming of the mixture to room temperature, measurement of pressure, cooling to $-210^{\circ}C$, and pumping. When a constant pressure is observed (usually after the third extraction), the gas remaining is NF_3 containing a small but detectable quantity of both CF_4 and SiF_4. Since neither are detectable by infrared spectra of the starting materials, it is assumed that they are derived from the reaction vessel. The impurities present, however, do not contribute appreciable error to the determination of F_2 and NF_3 from pressure readings obtained as described above.

The reactor is cut open with a hack saw within the dry box and the NF_4^+ antimonate and complex antimonate salts (> 15 grams) are safely removed from the reactor by breaking up the melt and scraping it out.

Reaction with SiO_2. Because water and the elements of water are extremely difficult to remove from glass, it was necessary to observe

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the interaction of NF_4SbF_6 with glass to determine the feasibility of obtaining X-ray powder diffraction patterns in glass capillaries. As expected, the reaction of very dry glass with NF_4SbF_3 resembled hydrolysis until the elements of water were depleted. When the temperature was increased to $85^\circ C$, a different reaction occurred, yielding I^- and SiF_4 but no oxygen. It was assumed that O_2SbF_6 was formed. At higher temperatures, the monel vessel was attacked and metal oxides were formed. Thus it appears that X-ray spectra can be obtained only with special treatment of th glass capillaries to avoid partial decomposition of the sample.

Reaction with Halides. Attempts to obtain infrared spectra in KBr, KCl, and AgCl showed that NF_4^+ reacts with bromide but not with these chlorides in the solid state.

NMR Spectra. F^{19} resonance spectra were obtained from NF_4SbF_6 dissolved in HF and contained in an FEP Teflon capsule. The capsule fits inside a standard nmr tube and had an i.d. of 0.100 in. The capsule permits diffusion of water vapor through its walls such that half the NF_4^+ is hydrolyzed after five weeks. The spectrometer is a Varian Associates Model HA-100, operated in the HR mode at 94.1 Mc/s.

Solubility in HF. NF_4SbF_6 is quite soluble in HF, 0.75 gram having completely dissolved in 1 gram of HF in an FEP Teflon vessel. The salt precipitated from solution, however, when exposed to a passivated monel vessel, indicating that it easily forms supersaturated solutions. Relative intensities of nmr lines show that solubility decreases with decreasing temperature.

Thermal Decomposition. NF_4SbF_6 is thermally stable at $200^\circ C$ but decomposes rapidly above $300^\circ C$ according to the reaction:

$$NF_4SbF_6 \longrightarrow NF_3 + F_2 + SbF_5$$

The decomposition was carried out in a monel vessel heavily passivated with respect to F_2 and SbF_5. The F_2 and NF_3 were recovered quantitatively in a 1:1 mole ratio (approximately 49% NF_3 and 48% F_2) but only a small quantity of the SbF_5 was observed, the balance having been taken up by the metal vacuum lines.

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The number of moles of NF_4^+ formed is equal to the number of moles of NF_3 consumed, because no other products from other reactions involving NF_3 have been detected.

In preparations involving the quantities of reactants given above at 200°C and 50 hours, about 41% of the NF_3 initially present is consumed. The consumption of NF_3 drops to 11% at 100°C for 50 hours. The amount of F_2 consumed always exceeds the amount of NF_3 consumed because of reaction of F_2 with the container.

The NF_4^+ salts react readily with moisture in the atmosphere but are stable indefinitely in the nitrogen atmosphere provided by a Vacuum Atmospheres Corporation dry box equipped with a recirculation system that removes both oxygen and water.

Hydrolysis. Weighed samples (0.5 gram) of the product were hydrolyzed in one to two cc of water. The hydrolysis is a smooth reaction proceeding according to the equation:

$$NF_4^+ + H_2O \longrightarrow NF_3 + \tfrac{1}{2}O_2 + H_2F^+$$
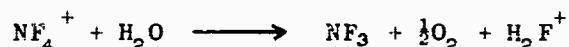
The NF_3 and O_2 were determined by the method described for NF_3 and F_2. The ratio of NF_3 to O_2 was 2 to 1 with a precision of 2 parts in 200. Mass spectrometric analysis of the gases evolved showed only NF_3 and O_2; no other gases such as nitrogen oxides were detectable. The hydrolysis of the anion(s) is complex and is comple n strong base.[8] The hydrolysate was later analyzed for antimony by bromate titration,[9] with the modification that borate was added to eliminate interference by fluoride ion. Fluoride was determined colorimetrically.[10] Because the product is contaminated with salts from the monel metal container, the sample is also analyzed for Ni^{+2} and Cu^{+2}. The contamination by copper which might reasonably be expected to occur in a monel vessel is usually negligible.

The elemental analysis performed as above indicates the presence of complex fluoantimonate anions. When the mixtures from various preparations were heated at 200°C for three days, they analyzed quantitatively from 96.0 to 99.5% NF_4SbF_6 and the balance $Ni(SbF_6)_2$. These purities

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represent a range observed in 12 preparations, and the quality of preparations improved as our work progressed.

Calc. for NF_4SbF_6: N = 4.30   Sb = 58.33   F = 37.37

Found: N = 4.27±0.04   Sb = 57.85±0.06   F = 37.64±1.5   Li < 0.30

Preparation of NF_4AsF_6. NF_3, F_2, and AsF_5 were heated at an initial pressure of 2000 psi for 260 hours at 125°C. About 12% of the NF_3 was converted to a solid product that, when heated to 300°C, decomposed to yield approximately equimolar quantities of the starting reagents. Hydrolysis of 0.5 gm of the salt yielded NF_3 and O_2 in an approximately 2 to 1 mole ratio. No oxides of nitrogen were detectable by mass spectrometry. The sample was about 95% pure.

RESULTS AND DISCUSSION

The interaction of NF_3, F_2, and SbF_5 has been studied in several reactions under varying conditions of temperature, pressure, and proportion of starting materials. The product is NF_4SbF_6 contaminated with a small percentage of metal antimonate salts from the reaction vessel. This conclusion is based on elemental analysis, identity and quantity of products from hydrolysis, thermal decomposition, and nmr spectra.

The results from elemental analysis rule out empirical formulas other than $NSbF_{10}$.

The F^{19} nmr spectra of the reaction product dissolved in HF (Figure 5) consisted of a triplet at -214.7 ppm from $FCCl_3$ and a broad line obscured by the sidebands downfield from HF. The latter appears to be characteristic of SbF_8^-, while the triplet differs from any known NF compound. The triplet was assigned to NF_4^+ as follows:

(1) The resonance triplet having lines of equal intensity can arise from the interaction of F^{19} with a nucleus having unit quadrupole moment. (2) The triplet no longer appeared after the product had been thermally decomposed and had evolved equivalent quantities of both NF_3 and F_2.

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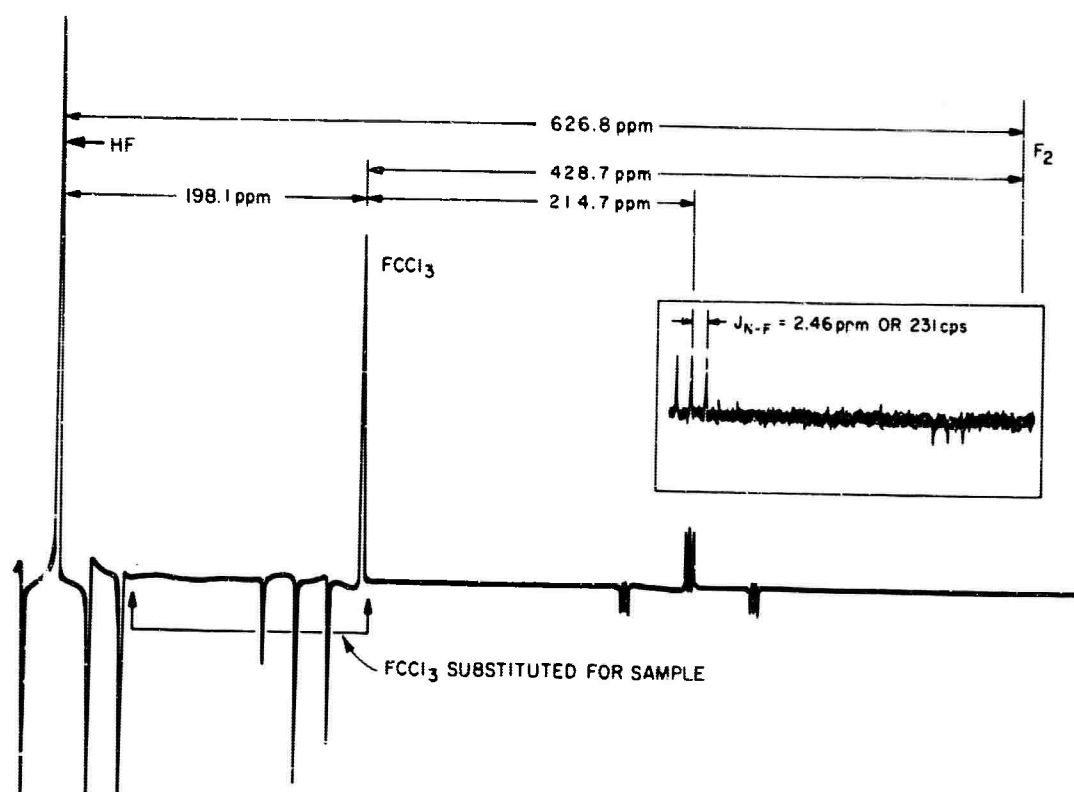
FIG. 5 NMR SPECTRUM OF NF$_4$SbF$_6$

TC-4466-21

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Thus since nitrogen has a quadrupole moment of one, the triplet is due to the presence of a structure of the type $NF_x^{\pm,0}$ Exclusion of paramagnetic structures and those having more than eight electrons in the bonding orbitals allows only NF, NF_2^-, NF_2^+, and NF_4^+. (3) The hydrolysis of the product evolves NF_3 and O_2 while NF_3, N_2F_2, and the ionic complexes N_2FAsF_6 (Ref. 11) and $N_2F_3Sb_2F_{11}$ all produce oxides of nitrogen, (The hydrolysis of the gases is slow, while that of the ionic compounds is rapid, $N_2F_3Sb_2F_{11}$ hydrolyzing explosively at room temperature.) In addition, evolution of NF_3 and O_2 in a ratio of 2 to 1 on hydrolysis shows that the oxidation number nitrogen in the allowed NF species is five. NF_4^+ is the only one of the allowed structures that has the proper valence and that could produce NF_3 on hydrolysis. If NF_4^+ is present as shown above, the compound has the structure $NF_4^+SbF_6^-$.

The existence of the NF/F^{19} triplet and no other resonance attributable to an NF structure shows that all fluorines in NF_4^+ are equivalent and that the structure of the ion is almost certainly tetrahedral as expected.

Fluorine nmr spectra were obtained on numerous reaction products as well as on products converted to NF_4SbF_6 by heating in vacuo.[12] No resonance lines other than those attributable to NF_4^+ in the form of its antimonate or complex antimonate salts have been observed. The combined evidence from nmr spectra, hydrolysis, and analysis of unreacted starting materials shows that NF_3 undergoes no reactions other than those leading to formation of NF_4^+. The reaction mechanism leading to NF_4^+ is not known, although it might involve either the heterolytic dissociation of F_2 to form $F^+SbF_6^-$, formation of NF_2SbF_6, or both.

The stability of NF_4SbF_6 in vacuo at 200^oC and its decomposition at 300^oC implies that the ion, at least in this salt, is quite stable. The latter indicates an activation energy (possibly 30 to 50 kcal/mole) for the decomposition of NF_4^+ that is higher than we expected and much higher than anticipated by Wilson.[8] Consequently, the hypothetical salts he discussed might very well have sufficient stability to be preparable.

ACKNOWLEDGMENTS

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(12) After learning that we had synthesized the NF_4^+ ion in the form NF_4SbF_6, Christe et al.[13] requested that we obtain nmr spectra from two samples of a powdery solid that had been prepared in a glow discharge reaction involving NF_3, F_2, and AsF_5 in a glass reaction vessel. When HF was added to the first of these, part of the white powder dissolved forming a colorless solution and part formed a dark brown residue that appeared to be copper fluoride. The colorless solution was decanted into an FEP Teflon nmr tube, and the spectra showed no NF species were present. A broad, intense resonance line due to AsF_6^- was observed upfield from HF, however, indicating the presence of a substantial quantity of AsF_6^- salts.

The second sample prepared subsequently from quantities of reactants exposed to glow discharge for several weeks was dissolved in HF and, as before, formed a colorless solution and a dark residue. The nmr spectrum contained, at very low intensity, the triplet we had shown earlier to be characteristic of NF_4^+. We estimated from

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[*]See Article 4 of this report.

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the ratio of the area of the hexafluoroarsenate line to that of
the triplet (about 100 to 1) that this particular sample almost
certainly contained about 1% NF_4AsF_6. The balance of the arsenic
salts were thought to be $NOAsF_6$ and NO_2AsF_6 formed by reaction
of fluorine with glass during the glow discharge. It was later
reported[13] that hydrolysis of the discharge product yielded nitrogen
oxides along with NF_3. The hydrolysis of $NOAsF_6$ could explain
the evolution of NO, while that of NF_4AsF_6 could not. This
difference in properties of NF_4AsF_6 indicates that the glow discharge
produced impurities at least in the samples we examined. These
observations, however, comprise a partial confirmation of our
conclusions in that the glow discharge synthesis is a third method
of preparing the NF_4^+ cation.

(13)   K.O. Christe, J.P. Guertin, and A.E. Pavlath, Inorg, Nucl. Chem.
       Letters, 2, 83 (1966).

ILLUSTRATIONS

Article 2

THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, NF_4^+

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THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, NF_4^+

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The purpose of this note is to report the first synthesis of the
tetrafluoroammonium ion, NF_4^+. The ion was synthesized in the form of
its salt, NF_4SbF_6, during research directed toward determining conditions
under which the ionic species, NF_x^+, can be made to exist. The approach
included studies of the system $NF_3/F_2/SbF_5/HF$ and its six binary and four
ternary subsystems, whose reactions forming solid salts in these systems
possibly involved the following:

$$1. \quad NF_3 + SbF_5 \xrightarrow{HF} NF_2SbF_6$$

$$2. \quad NF_3 + HSbF_6 \xrightarrow{HF} HNF_3SbF_6$$

$$3. \quad NF_3 + F_2 + SbF_5 \xrightarrow{HF} NF_4SbF_6$$
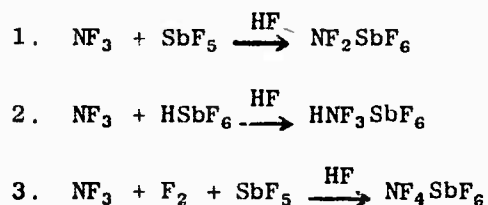
At ambient and lower temperatures and at pressures up to 12 atmospheres,
we observed no new N-F-containing species in the systems containing NF_3
either by means of conductivity and solubility measurements or by means of
NMR and EPR spectra. In addition, thermochemical estimates indicated that
the heat of reaction to form the hypothetical crystal, NF_4^+/F^-, would be
endothermic by about 50 kcal. More significant, perhaps, is that the
several mechanisms through which NF_4^+ itself might be formed involved
processes considerably more endothermic than indicated by the net heat
of reaction. [1,2]

From prior experimental observations, thermochemical estimates, and
the calculations of Curtis and Wilson[2] on the estimated entropy and
stability of the NF_4^+ cation, it seemed reasonable that the synthesis of

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NF_4SbF_6 could be accomplished by heating the quaternary system, $NF_3/F_2/SbF_5/HF$, at moderate temperatures and relatively high pressures. The synthesis occurred as expected when equimolar quantities of NF_3, F_2, and SbF_5 were heated in a monel tube reactor for about 2-1/2 days at $200^{\circ}C$ and at pressures up to 85 atmospheres. A liquid phase of HF and SbF_5 was present at a concentration of 0.2 mole fraction of SbF_5 relative to HF at room temperature. On completion of the reaction and removal and analysis of unreacted starting materials, the solids remaining in the reactor exhibited a vapor pressure not in excess of a few microns at $200^{\circ}C$. The product was decomposed at $350^{\circ}C$ in vacuo yielding approximately 0.01 mole of gas containing equimolar quantities of NF_3 and F_2. In this first experiment, no attempt was made to observe SbF_5. The evolution of equimolar quantities of NF_3 and F_2 was expected from the thermal decomposition of NF_4SbF_6 formed as shown in reaction (3).

Reaction parameters have been studied, and it appears that a satisfactory preparation is obtained when 0.1 mole each of NF_3, F_2, and SbF_5 (the latter 0.2 mole fraction in HF) are heated at $200^{\circ}C$ for two to three days in a 60 cc monel tube reactor and at pressures up to 18 atmospheres. The crude product also contains salts formed by the reaction of monel metal with F_2 and SbF_5. We have, in fact, been unable to obtain any evidence that the crude product contains other than a mixture of NF_4SbF_6 and the salts from the reaction with monel metal.

From material balances on a number of preparations, the consumption of NF_3, F_2, and SbF_5 was best accounted for by the formation of NF_4SbF_6 along with Ni(II) and Cu(II) hexafluoroantimonates. In a typical preparation, more than 40% of the NF_3 charged is converted to a solid. The crude product of the reaction contains about 0.035 mole of NF_4SbF_6 and is approximately 75% pure by weight, the remainder consisting of metal salts. The crude (75%) NF_4SbF_6 was characterized without further purification by means of thermal decomposition, hydrolysis, and F^{19} NMR spectra. Above $300^{\circ}C$ thermal decomposition proceeded according to the following reaction:

$$NF_4SbF_6 \xrightarrow{\Delta} NF_3 + F_2 + SbF_5$$

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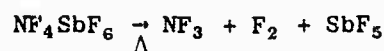
The hydrolysis reaction was:

$$NF_4SbF_6 + 7H_2O \rightarrow NF_3 + \tfrac{1}{2}O_2 + HSb(OH)_6 + 7HF$$

Hydrolysis proceeds smoothly to yield a colorless solution. Data from these reactions agreed within experimental error with the product composition indicated by the material balance. The NMR spectra of the HF solution of the product contained a triplet resonance, centered at -214.7 ppm from $FCCl_3$. The lines of the triplet were equally intense with a coupling constant, J_{N-F}, of 231 cps. The chemical shift and splitting differ from any known N-F species. These observations and others not included in this note are consistent with the synthesis, reactions, and properties of the salt, NF_4SbF_6.

Subsequently, the salt, NF_4AsF_6, was synthesized by the same method used for the synthesis of NF_4SbF_6. The conversion of NF_3 was substantially less, apparently because of the volatility of $Ni(AsF_6)_2$ at $200^{\circ}C$. The product decomposed at $300^{\circ}C$ to yield NF_3, F_2, and AsF_5.

It was most gratifying to have certain of the results reported here confirmed in research conducted at the Stauffer Chemical Company by Christe, Guertin, and Pavlath.[3] At their request, we obtained NMR spectra from samples of two solids which they had prepared in a glow discharge in the presence of NF_3, F_2, and AsF_5. The N-F resonance which we had earlier shown to be characteristic of NF_4^+ was observed at low intensity in the HF-soluble portion of one of the two samples. Their glow discharge product almost certainly contained NF_4AsF_6.

ACKNOWLEDGEMENTS

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2. R.M. Curtis and J.N. Wilson, pp 2J, Abstracts of Papers presented at the 149th Meeting of the American Chemical Society, Detroit, Michigan, April 1965.

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Article 3

EVIDENCE FOR THE EXISTENCE OF THE $Sb_2F_{11}^-$ ANION

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EVIDENCE FOR THE EXISTENCE OF THE $Sb_2F_{11}^-$ ANION

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ABSTRACT

In a study of the strongly acid system HF/SbF_5, F^{19} nmr spectra consistent with the presence of H_2F^+, SbF_6^-, and the structure $Sb_2F_{11}^-$ were obtained on mixtures that were about 0.2 mole fraction SbF_5. The $Sb_2F_{11}^-$ structure is that of two octahedra joined by a common apex. The resonance lines assigned to $Sb_2F_{11}^-$ were resolved at a temperature just above the freezing point of the mixture near $-50^\circ C$. A stable salt of this anion, $NF_4Sb_2F_{11}$, was also synthesized and characterized.

NOTE

In a study of the system HF/SbF_5, by means of conductivity measurements and infrared and Raman spectra, Hyman et al.[1] established the equilibrium reaction

$$2HF + SbF_5 \rightleftarrows H_2F^+ + SbF_6^-$$

They also concluded from their evidence that another discrete species was present and suggested that it might be the ion pair $H_2F^+SbF_6^-$. We

have obtained evidence from F^{19} nmr spectra of the HF-SbF_5 system that this species is probably $Sb_2F_{11}^-$. The F^{19} nmr spectra of this system were observed elsewhere independently, and the $Sb_2F_{11}^-$ ion was similarly deduced.[2] These independent results have not, however, been published. In addition, we have observed the formation of a salt $NF_4Sb_2F_{11}$ that contains this anion. A similar salt $N_2F_3Sb_2F_{11}$ also appears to have this structure.[3]

Fluorine resonance spectra were obtained on mixtures that were approximately 0.05, 0.2, and 0.5 mole fraction SbF_5 in polychlorotrifluoroethylene nmr tubes at ambient temperature and at temperatures just above the freezing point of each mixture. For the samples that were 0.2 mole fraction in SbF_5, this temperature was about $-50^{\circ}C$. In normal operation, the Varian Associates HA-60 Spectrometer produced spectra having sidebands that overlapped and obscured the observed resonance lines of the HF/SbF_5 system. The sidebands were eliminated by disconnecting the integrator, and it then became necessary to record data by photographing the spectra displayed on the oscilloscope screen.

The spectra of all mixtures at ambient temperature consisted of very broad lines, but at just above the freezing point of the mixture that was 0.2 mole fraction SbF_5, five relatively sharp lines were observed: three of these had fine structure. Data derived from these spectra are given in Figure 1. The chemical shifts of the lines were obtained by calibrating the horizontal scale of the oscilloscope grid in parts per million per division. This was done by using the chemical shifts of pure antimony pentafluoride[3] and pure HF from $FCCl_3$ as references. We estimated that the shifts of the observed lines were obtained within four ppm.

In view of the presence of SbF_6^- and H_2F^+ as shown by Hyman et al., two of the five lines were attributed to these species. In Figure 1, peak I was most probably due to SbF_6^- and peak II to the exchange between HF and H_2F^+.

The spin coupling splittings in the fine structure observed in the three remaining peaks were determined with the aid of a 100 cps sideband. These splittings, shown in Figure 1, indicate that the three lines are

related to a single-species. The areas of the three lines are best expressed in terms of the ratio 1:8:2, corresponding to peaks labeled A_1, M_8, and X_2 in Figure 1. While the areas could not be determined with sufficient precision to rule out other closely related ratios, the ratio 1:8:2 was consistent with the species $Sb_2F_{11}^-$ in the form of two octahedra joined by a common apex. The quadruplet labeled M_8 resembled a pair of overlapped doublets and was consistent with eight equivalent fluorines split by two types of non-equivalent fluorine. The quintuplet X_2 appeared as a regular binomial distribution and was consistent with two equivalent fluorines split by four. Finally, although A_1 was observed as a seven-fold multiplet instead of the nine-fold array required by this structure, it is still consistent with the splitting of a single fluorine by eight equivalent ones. This follows from the binomial distribution of intensities that predicts the first and last lines of a multiplet of nine to be $1/168$ of the intensity of the central line. Thus, in this method of obtaining spectra from the oscilloscope screen, sufficient amplification could not be used to observe them.

While this evidence satisfactorily indicated the presence of $Sb_2F_{11}^-$ in the HF/SbF_5 systems, it remained to observe the existence of salts having this anion. This occurred in studies which followed the synthesis[4] of NF_4SbF_6 from the reaction of NF_3, F_2, and SbF_5 under high pressure and at 100 to 200°C. At 100°C and in the presence of excess SbF_5, the product formed in this reaction is $NF_4Sb_2F_{11}$ as shown by elemental analysis. It is stable at 100°C in vacuo but loses SbF_5 to form NF_4SbF_6 at 200°C.

The synthesis of the salt $NF_4Sb_2F_{11}$ and the nmr spectra consistent with the $Sb_2F_{11}^-$ structure taken together comprise substantial evidence for the existence of the $Sb_2F_{11}^-$ ion.

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FIGURE LEGEND

Fig. 1. Fluorine nmr spectra of the HF/SbF_5 system.
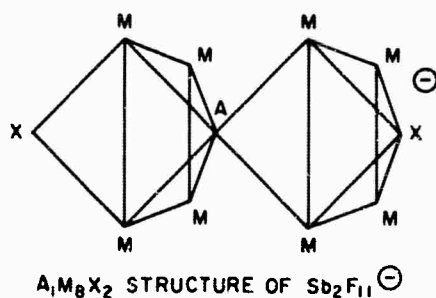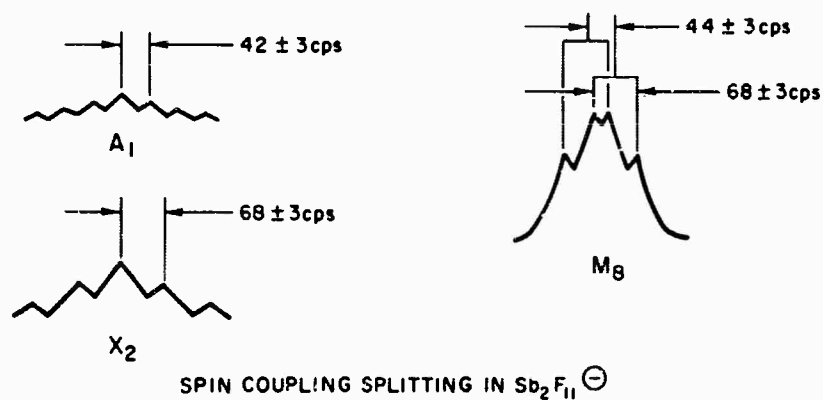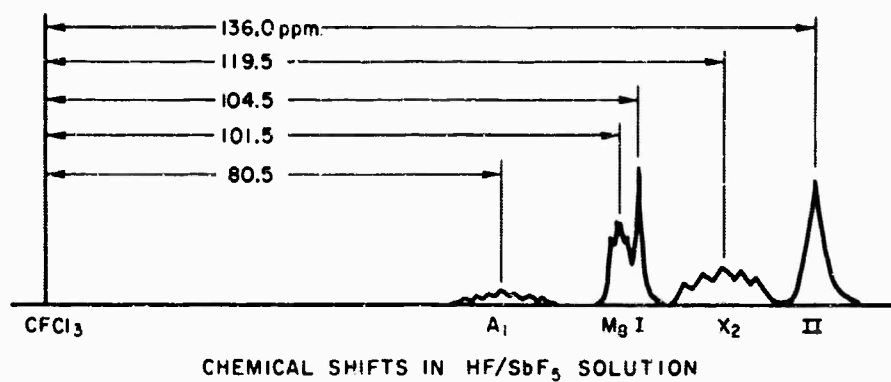
CHEMICAL SHIFTS IN HF/SbF₅ SOLUTION

SPIN COUPLING SPLITTING IN Sb₂F₁₁⁻

A₁M₈X₂ STRUCTURE OF Sb₂F₁₁⁻

FIG. 1 FLUORINE nmr SPECTRA OF THE HF/SbF₅ SYSTEM

Article 4

THE SOLUBILITY OF F_2, AND O_2 IN ANHYDROUS LIQUID HF

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THE SOLUBILITY OF F_2, NF_3, AND O_2 IN ANHYDROUS LIQUID HF

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ABSTRACT

The solubilities of F_2, NF_3, and O_2 in anhydrous liquid HF have been measured at several temperatures. The solubility of F_2 passes through a minimum between 0 and 20°C. The solubility of NF_3 exhibited no such minimum in the temperature range studied but deviated appreciably from ideal behavior at dry ice temperature and above one atmosphere pressure. The solubility of O_2 was measured at 0 and 20°C. and was, as expected, virtually identical with that of F_2. In contrast, the solubilities of O_2 in HF at 0 and 20°C. were factors of ten and five, respectively, larger than the literature values of the solubility of O_2 in H_2O at the corresponding temperatures.

Solubilities of gases in liquids are of theoretical interest, and when measured with sufficient precision and sensitivity, can be used along with other information such as conductivity to infer the presence or absence of interaction of the gas with the solvent. In the study of the chemistry of NF_3 and F_2 in liquid HF, it was of interest to determine their solubilities in this solvent. The solubility of O_2 in HF was also determined in order to permit comparison between solubilities in HF and in H_2O. A similar comparison of the solubilities of F_2 in the two solvents would have little value because of the reaction of F_2 with water.

The solubility of BF_3 in liquid HF is the only recently reported[1,2,3] gas solubility in HF. Thus, this paper is the first report of the solubilities of F_2, NF_3, and O_2 in HF. The method used in this work was

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similar to that used by Kilpatrick and Luborsky,[1] and the measurements were made at several temperatures from 19.85 to -77.2°C.

EXPERIMENTAL SECTION

The apparatus used is shown in Figure 1. All parts were fabricated from Monel metal and were assembled by brazing with silver solder. All valves were Hoke M-482-M bellows valves. The volumes of vessels were determined from the weight and density of distilled water that completely filled them. Volumes of the reaminder of the system were calculated from PV changes of argon. Two Wallace and Tiernan pressure gages were used: a 0-1520 mm. gage and a dual-scale gage, 0-200 psia and 0-1035 cm. Hg. Both had calibrations traceable to the Bureau of Standards but were tested as follows: the low pressure gage agreed exactly with a mercury barometer at atmospheric pressure. Successive quantities of argon measured at one atmosphere were then condensed into the high pressure gage volume. Assumption of the perfect gas law permitted calculation of the pressures that should have resulted. The standard deviation of the pressures observed from those calculated was 0.7 cm. Hg.

Anhydrous hydrogen fluoride was obtained in excellent purity from Olin Corporation. It was condensed into a copper trap at liquid nitrogen temperature and pumped on to remove hydrogen. The HF was then distilled slowly into a Kel-F conductivity cell having platinum electrodes and was found to have a conductivity of 3×10^{-5} ohm.$^{-1}$ cm.$^{-1}$, indicating relatively high purity. The HF was then distilled into the 450 cc. vessel and weighed: 212.9 grams were present.

Flurine was obtained from Allied Chemical Corporation with a typical analysis of 98% purity. It was purified by condensing a known quantity of gas into a trap packed with nickel spirals and cooled to -190°C Gases volatile at -190°C. were then transferred to a receiver at -196°C. The significant impurity remaining is approximately 1% air. A substantial part of the remaining air was removed by extractions of the vapor above the liquid fluorine into an evacuated volume. The fluorine obtained in this manner was used without further purification or analysis.
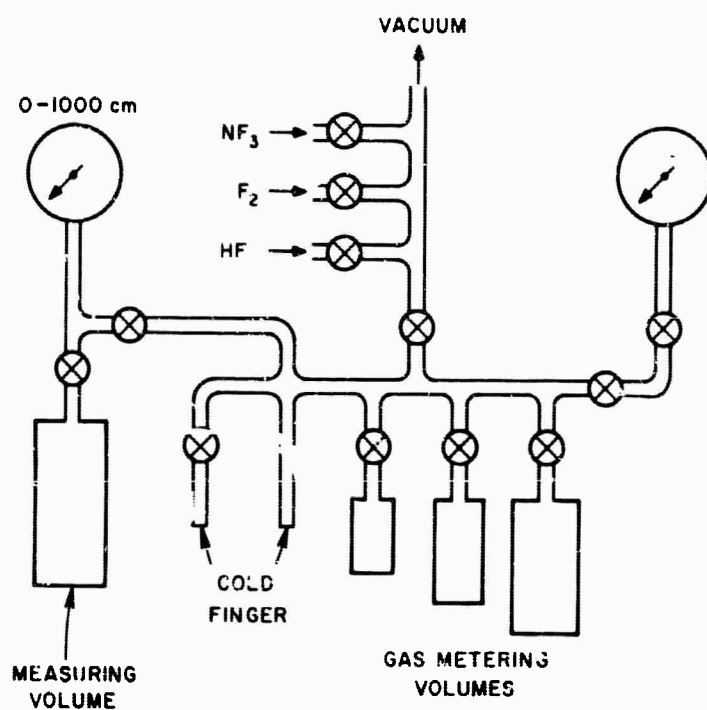
FIG. 1 SOLUBILITY APPARATUS

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RESULTS

The solubility of F_2 in HF at five temperatures is given in Figure 2. The straight line plots are given by a Henry's law expression, $p = kM$, wherein the pressure of fluorine in the vapor phase equals a constant times the molality of fluorine in solution. The solubility apparently goes through a minimum between 0 and $20^{\circ}C$., but between 0 and $-77.2^{\circ}C$. the solubility can be calculated from the temperature coefficient. Values calculated from the latter agree within 3% of the values determined in single point measurements at -23 and $-65^{\circ}C$.

The solubility of NF_3 at three temperatures is shown in Figure 3. Straight line plots were obtained at ice temperature and above. At dry ice temperature, a curved plot was observed. Its limiting slope was very nearly equal to that predicted from the temperature coefficient from which the calculated curve was derived. From this fact, it seems clear that NF_3 does not have a solubility minimum in t : temperature range observed and that the nonlinearity of the solubility at dry ice temperature might be due to other effects such as hydrogen bonding between HF and NF_3, or to intereactions of NF_3 with itself at a temperature and pressures c? so to critical. The latter seems most likely.

The solubility of O_2 in HF is given by $p = 3.4 \times 10^3 M$ at $293.0^{\circ}K$. and $3.320 \times 10^3 M$ at $272.9^{\circ}K$., where p is in cm. Hg. M is in moles per 1000 grams, and k in corresponding units.

The solubilities of O_2 and F_2 in HF are very similar at ice temperature and $20^{\circ}C$. Because the solubility of O_2 was not studied at additional temperatures, no conclusions as to the existence of a solubility minimum can be made, nor is it likely that solubilities can be estimated reliably by extrapolation of the temperature coefficient.

Comparison of the solubility of O_2 in HF and in H_2O^3 shows that it is a factor of ten less soluble in H_2O at $0^{\circ}C$. The solubility of F_2 in water is probably similarly a factor of ten less.

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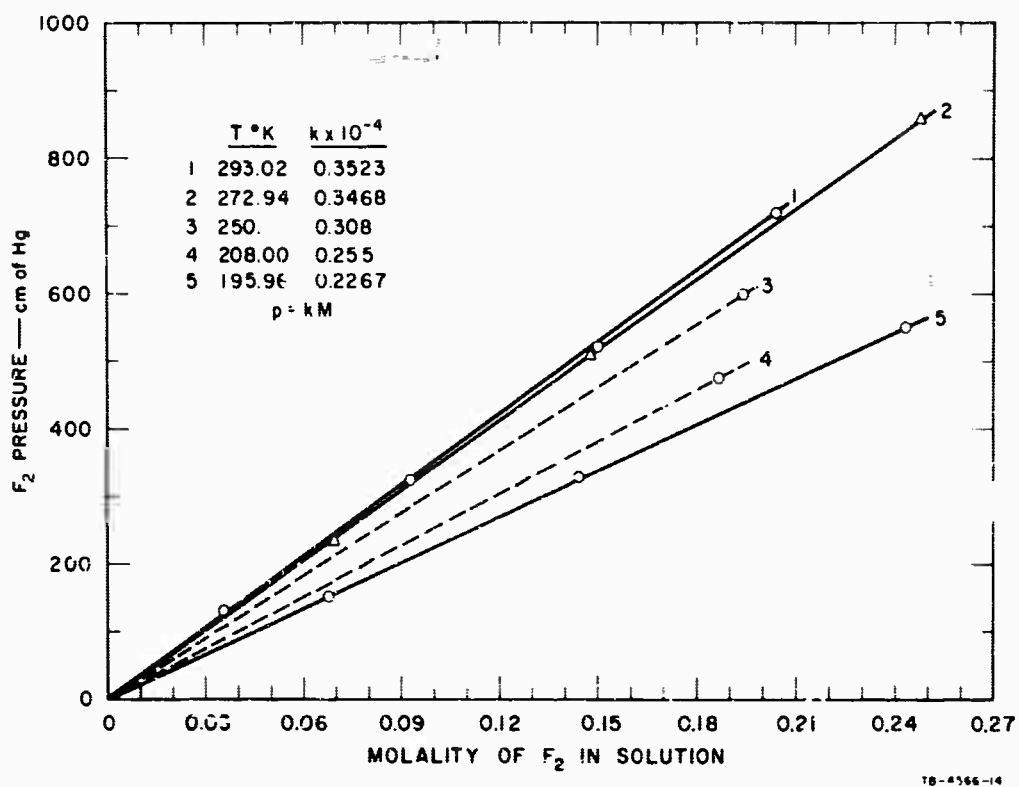
FIG. 2 SOLUBILITY OF FLUORINE IN HF AT FIVE TEMPERATURES
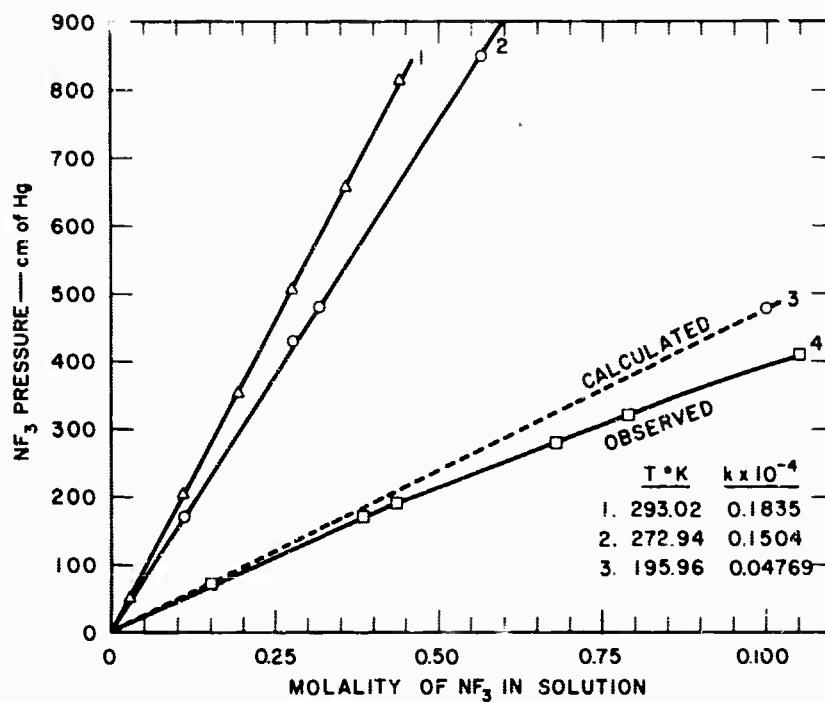
FIG. 3 SOLUBILITY OF NF$_3$ IN HF AT THREE TEMPERATURES

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FIGURE LEGEND

Figure 1.   Solubility Apparatus

Figure 2.   Solubility of Fluorine in HF at Five Temperatures

Figure 3.   Solubility of NF_3 in HF at Three Temperatures

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	Air Force Rocket Propulsion Laboratory

13. ABSTRACT   Articles 1 and 2

When a mixture of nitrogen trifluoride, fluorine, and antimony pentafluoride is heated under pressure, the salt NF_4SbF_6 is formed. This is the first derivative of the perfluoroammonium cation NF_4^+ to be observed. It was characterized by evidence obtained from thermal decomposition, hydrolysis, elemental analyses, and fluorine nmr spectra. The salt is stable in a very dry atmosphere and at $200°C$ <u>in vacuo</u> but decomposes rapidly above $300°C$ to NF_3, F_2, and SbF_5. Elemental analysis was carried out by determination of the quantity and identity of the gases evolved on hydrolysis followed by analysis of the hydrolysate. Hydrolysis of NF_4^+ quantitatively produces NF_3 and O_2 in a two to one mole ratio. These analyses showed that the empirical composition of the solid was $NSbF_{10}$, and that the oxidation number of nitrogen in the compound is five. The product is from 96 to 99% pure as isolated from the monel reactor, the balance consisting mainly of $Ni(SbF_6)_2$. The fluorine nmr spectra were obtained from the salt dissolved in anhydrous HF and were consistent with the presence of SbF_6^- and of a species of the type $NF_x^{\pm,0}$. From this and other evidence the structure of the salt was shown to be $NF_4^+SbF_6^-$. Because the nmr spectra showed that all fluorines attached to nitrogen are equivalent, the NF_4^+ ion is almost certainly tetrahedral.

The salt NF_4AsF_6 was also synthesized in a similar reaction and was characterized by thermal decomposition, hydrolysis, and elemental analysis. These results were quite analogous to those of the antimonate salt except that the thermal decomposition temperature was slightly lower and the purity was only about 95%.

(Abstracts continued)

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14		LINK A		LINK B		LINK C	
	KEY WORDS	ROLE	WT	ROLE	WT	ROLE	WT
NF_4^+ cation							
Sb_2F_{11} anion							
HF Solution Chemistry							
Solubility of gases in liquid HF							

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Article 3

In a study of the strongly acid system HF/SbF$_5$, F^{19} nmr spectra consistent with the presence of H$_2$F$^+$, SbF$_6^-$, and the structure Sb$_2$F$_{11}^-$ were obtained on mixtures that were about 0.2 mole fraction SbF$_5$. The Sb$_2$F$_{11}^-$ structure is that of two octahedra joined by a common apex. The resonance lines assigned to Sb$_2$F$_{11}^-$ were resolved at a temperature just above the freezing point of the mixture near -50°C. A stable salt of this anion, NF$_4$Sb$_2$F$_{11}$, was also synthesized and characterized.

Article 4

The solubilities of F$_2$, NF$_3$, and O$_2$ in anhydrous liquid HF have been measured at several temperatures. The solubility of F$_2$ passes through a minimum between 0 and 20°C. The solubility of NF$_3$ exhibited no such minimum in the temperature range studied but deviated appreciably from ideal behavior at dry ice temperature and above one atmosphere pressure. The solubility of O$_2$ was measured at 0 and 20°C. and was, as expected, virtually identical with that of F$_2$. In contrast, the solubilities of O$_2$ in HF at 0 and 20°C. were factors of ten and five, respectively, larger than the literature values of the solubility of O$_2$ in H$_2$O at the corresponding temperatures.